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The Degradation of Crude Oil in Northern Soils

Northern Affairs Program

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ABSTRACT

Following the accidental spillage of crude oil or petroleum products on arctic terrain there is usually an immediate herbicidal effect, followed by a period of some years during which the oil weathers and degrades slowly and loses its toxic components. Eventually vegetation becomes re-established and the site probably recovers to its original condition. This report reviews the many physical and biological processes which cumulatively determine the rate at which the oil is degraded, and hence control the duration of the recovery period. Also reviewed is the feasibility and desirability of enhancing recovery rates by artificial measures such as containment, fertilizing, or burning.

The results of several experimental studies are reported and their implications discussed. These include observations and analyses made at oil spill sites at Norman Wells, Inuvik, Tuktoyaktuk and Richards Island (NWT). Results are presented of the recovery rates of a series of experimental spill sites in Southern Ontario. A laboratory study of oil evaporation rates from soils is described in which equations have been developed and validated which permit these rates to be calculated for the first time. Sampling and analytical procedures have been developed for improved sampling and monitoring of oiled soil sites. A novel vapour extraction procedure has been devised to permit quantitative recovery of volatile soil components.

It is believed that the dominant oil detoxifying processes are evaporation and biodegradation. The physical-chemical condition of the soil may also be very important since oil tends to render surfaces hydrophobic thus reducing water retention. Measures are reviewed which can be taken to enhance the rates of these processes, for example aerating and fertilizing. Under some conditions burning may be a useful countermeasure, especially if the soil is frozen or water-logged.

The implications of the results for enhancing rehabilitation of oiled sites are discussed and recommendations are made for procedures for mitigating the effects of oil spills on arctic terrain.

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1. INTRODUCTION

This report is concerned with elucidating the physical processes which occur when crude oil or a petroleum product is spilled on northern soils, especially those which may be underlain by permafrost. It also examines the issue of physical rehabilitation practices which may enhance the rate of recovery.

In the last 10 years there has developed a considerable body of information about the behaviour of oil spills on land. Examples are the works of Mackay et al (1975) on the physical behaviour of the oil, Hutchinson and Hellebust (1978), and Bliss (1972) on the effects on vegetation, Parkinson et al (1975) on soil microflora, and Cook and Westlake (1975), Westlake et al (1978) and Davies and Westlake (1979) on soil microorganisms and biodegradation. Most of these studies have been of small experimental spills. The greatest number of well documented spills have been in Alberta on temperate soils, as reported by McGill (1977), and Rowell and McGill (1978). Also relevant are the works of Cresswell (1977) on quantifying the rates of petroleum refinery oily sludge degradation on land disposal sites and of Vonhoff (1977) on movement of oil in groundwater as a result of leaking petroleum storage tanks.

With the advent of oil transportation by pipeline across Alaska, there has been a surge of interest in the effects of oil on northern terrain. Notable in this regard is the work of Walker et al (1978), Jenkins et al (1978), Sexstone et al (1978), Linkins et al (1978) and Everett (1978) on effects of oil on soils and plant communities; that of McKendrick and Mitchell (1978) on burning, and on fertilizing and seeding practices. In addition some practical experience resulting from actual spills from the Trans Alaska Pipeline has been reported by Allen (1979) and Buhite (1979). Reports on the merits of burning as a cleanup measure have been discussed by Vandermeulen and Ross (1977), McKendrick and Mitchell (1978) and Day et al (1979).

The major incentive for this work lies in the general acceptance of the principle that when oil is accidentally spilled on terrain, it should be cleaned up and the area rehabilitated as completely as possible, and as soon as possible, to its original state. Whereas "brute force" mechanical methods, such as bulldozing or burying may be acceptable in the south, more subtlety is needed in the north because of the risk of erosion from terrain disturbance and slower vegetation recovery rates. A variety of techniques are available, including tilling, fertilizing, seeding with microorganisms, flooding, burning and replacement or burial of the oiled soil. It seems likely that some selection or combination of these techniques will be appropriate for Arctic conditions and that ultimately pragmatic procedures can be recommended for spill site rehabilitation. The emerging conventional wisdom is that in the north it is better to avoid mechanical disturbances, but enhance where possible the natural recovery processes.

2. OIL BEHAVIOUR IN NORTHERN SOILS - A REVIEW

2.1 Short Term Behaviour of Oil Spills

As a result of work undertaken under the Environmental-Social Program Northern Pipelines, a fairly clear picture has emerged of the short term behaviour of crude oil spills on northern terrain (Mackay, Charles and Phillips 1975). A brief review of the salient points of oil flow in soils provides a useful background for this study.

The terrains of greatest interest are taiga and tundra regions which are characterised by a layer of living vegetation (mainly mosses and grasses) overlying a layer of organic detritus or litter, which in turn lies on a base of mineral soil or rock. Much of the area is underlain by permafrost in which the active layer depth varies from a few tens of centimetres to a metre or more. In winter, the ground is frozen and usually has a snow covering of variable thickness and density. During spring, the snow melts rapidly and there is a period of very high water runoff and flooding. The frost line or $0^{o}C$ isotherm undergoes an annual excursion from the surface in late May to a maximum depth in late August. In summer, there is a flow of groundwater through the soil. The nature of this flow depends on local hydrological conditions and recent rainfall. Because the underlying permafrost is relatively impermeable to water, much of the terrain is water-logged and there are commonly numerous small lakes and ponds.

The behaviour of an oil spill on this terrain is dependent on the season of the spill. In summer, which accounts for about 37% of the year, the oil will flood the moss and detritus layer permeating vertically downwards in a few minutes until it reaches a barrier which is either groundwater, impermeable soil, or frozen ground. Oil will flow on the surface and through the subsurface soil, possibly displacing some groundwater. The area affected by the spill will depend upon the topography, the absorptive capacity of the soil, and on the local topography. Areas contaminated by a large quantity of oil will probably retain about 0.1 m^3 of oil per m^2 of the area corresponding to a "depth" of about 10 cm of oil. This zone will be surrounded by a subsurface contaminated zone containing less oil - possibly about 5 cm depth. It is emphasised that these quantities could vary by a factor of 2 to 3 in both directions depending on local conditions.

In winter, which can be regarded as 55% of the year, the oil will be cooled rapidly, will increase in viscosity and its spreading velocity will be reduced by the barrier effect of snow. Much of the oil will remain on the surface rather than permeate to depth in the soil. The oil thickness will generally lie in the range of 5 to 17 cm and much will remain absorbed in snow. This oil will have the opportunity of weathering and by spring will probably be in a fairly viscous and weathered state. In zones close to the spill where the oil is hot it is likely that it will permeate more deeply into the soil.

Finally, in spring which represents about 8% of the year, it is likely that the oil will spread very rapidly assisted by moving water, and will thin out to a depth of about 1 cm. Much of the vegetation will be substantially under water and will thus be protected from the oil. The depth of the contamination will be approximately 1 cm.

Experimental spills have shown that the oil becomes immobile in a few hours. The oil coats the soil material and increases in viscosity due to evaporation and stops flowing. In the following weeks and years, the oil is subject to a number of processes collectively termed "weathering" which includes evaporation, dissolution into groundwater, biodegradation, possibly photolysis (near the surface), and chemical conversion. These processes generally render the oil more asphalt-like in character. There may be a misconception that oil must "mineralize" or degrade completely to carbon dioxide and water before it becomes totally innocuous. As oil weathers, it becomes increasingly inert chemically and biologically until it reaches a stage when it is essentially indistinguishable from organic detritus. At this stage, possibly as much as half of the original oil mass may remain. The period of interest and concern is thus the time from the spill to the point at which the oil becomes inert or biologically inactive and not the (longer) total time for conversion to carbon dioxide.

Following the spill, the area may be subjected to clean-up and/or rehabilitation attempts such as soil removal, oil burning (insitu or in incinerators), water flooding or burial. In this report we do not consider processes which remove, modify or bury the oil, but rather focus on those processes which occur naturally or are procedures which are designed to enhance the natural recovery rate. The most likely such procedures are burning and water flooding to "float" oil from the depths of the soil to the surface. Little information is available on the feasibility or effectiveness of either technique. It seems likely, however, that both techniques would have to be applied shortly after the incident occurs and before the oil has had the opportunity to evaporate substantially, because weathering increases viscosity and decreases the possibility of dislodging the oil from the soil fabric on which it is trapped, and burning will become impossible after loss of volatiles.

It is important to obtain some understanding of the relative rates of weathering processes in order that strategies can be developed for enhancing the natural recovery rates. Each process is discussed briefly below.

2.2 Dissolution and Dispersion

Most hydrocarbons have very low solubilities in water, the exceptions being the lower aromatics such as benzene, toluene and xylenes which have solubilities of 100 to 1800 mg/litre. Most alkanes with carbon numbers above C_6 have solubilities of the order of 1 mg/litre or lower. A typical fresh crude oil will have a total solubility of about 30 mg/litre but after evaporation, the solubility drops to about 1 mg/litre (Mackay and Shiu 1975). Dissolution may be important early in the spill history when volatile aromatics are present in high concentrations, but it is likely that evaporation is more important. Calculations of mass loss by dissolution suggest a maximum extent of dissolution of the order of one percent of the oil mass, although some oil which penetrates deeply into the soil and is exposed to a continuing groundwater flow and shielded from evaporation may lose its volatile and soluble components predominantly by dissolution. This contaminated groundwater may have significant toxic potential. (Miller et al, 1978)

In addition to dissolution is the even less understood process of

dispersion or oil-in-water-emulsion formation in which small oil drops in the range 0.1 to 10 μm diameter become separated from the main oil mass and flow with the water. Their formation is enhanced by surface active agents which may be present in the soil or the oil.

2.3 Biodegradation

The kinetics and mechanism of this process are not considered in detail in this report and reference can be made to other work, particularly that of Cook and Westlake (1975) and Parkinson et al (1975). Presumably the rate of biodegradation depends on factors such as the nature of the oil, the number and types of microorganisms, the presence of nutrients and oxygen, the temperature and the availability of other substances in which the microorganisms can grow. No attempt is made here to predict these rates but in the monitoring program an attempt has been made to measure the contribution of this process by measurement of the ratio of (slowly degradable) isoprenoid to (rapidly degradable) alkanes.

2.4 Chemical and Photochemical Conversion

Hydrocarbons are generally regarded as being chemically inert although some components containing nitrogen, sulfur or oxygen functional groups and some unsaturates may be quite susceptible to hydrolytic or oxidative conversion. The compounds of greatest relevence here are the lower alkanes and aromatics which are unlikely to experience such reactions. The reason for this inertness lies in the fundamental difficulty of breaking the relatively strong carbon-hydrogen or carbon-carbon bonds. Most reactive species present in the environment have insufficient energy to overcome the activation energy barrier necessary for cleavage. The exception is a series of active oxygen compounds such as ozone or singlet oxygen or free radical oxides or peroxides, which may be formed photolytically. It is believed that these compounds are mainly responsible for the conversion of hydrocarbons in the atmosphere into oxygenated degradation products. It is also possible that oil exposed to solar radiation absorbs photons and becomes activated and thus subject to reaction. Only recently has the significance of photolytic processes in the environment become fully appreciated, (Zepp and Baughman (1977)). It is possible that in some cases photolytic "softening-up" of oil is a precursor to biodegradation. A common observation is that surface oil exposed to sunlight degrades rapidly whereas oil trapped at depths degrades only slowly. This may also be due to temperature, lack of oxygen, slower evaporation or lower numbers of microorganisms, but it is difficult to separate these factors.

2.5 Evaporation

A knowledge of evaporation rates of oil impregnated in Arctic soils is useful or even essential because it is generally accepted that the volatile components of the oil tend to be the most "toxic" to vegetation. The loss of these compounds thus influences the total "toxicity" of the oil and it can be postulated that site rehabilitation will not be possible until some significant fraction of these toxic compounds has degraded or evaporated. The discussion below gives an account of the factors which are believed to influence the evaporation process.

Crude oil is a mixture of a very large number of hydrocarbons and other compounds. In theory, from a knowledge of the composition of the oil

and the properties of the individual components, one could calculate its evaporative character. In practice, this is impossible because there is little information about the composition and few data are available on component properties. The evaporation process leads to a loss of the lighter, more volatile material, which results in an increase in oil viscosity and density and there is a possibility of "skin" or "crust" formation which may impede subsequent evaporation. The rate of evaporation is also influenced by the degree of mixing in the oil film, i.e., the rate of transport of oil from the bulk to the surface. Thus oil thickness is a critical parameter in any evaporation process. Unfortunately, there is little information about the actual thicknesses which apply in soils. Evaporation is influenced by the level of atmospheric turbulence in the vicinity of the oil as expressed by a mass transfer coefficient. Values are available in the literature for mass coefficients for evaporation of pools of oil, however, no data are available for oil evaporation from the interstices of a soil.

Temperature provides an additional complication in that it affects vapour pressure and hence evaporation rate. In soils, it is difficult to determine or estimate an average temperature, because temperatures change diurnally and seasonally. This problem is particularly important in the Arctic soils where the temperatures at depths are close to or below 0°C for much of the year. Average temperatures are misleading, since vapour pressure is a nonlinear function of temperature and it is better to calculate a mean vapour pressure.

As the 0°C isotherm migrates from the surface in the spring to a depth of tens of centimetres by August, the depth of soil exposed to evaporation increases, and the temperatures steadily increase. Thus oil trapped deep in the soil generally experiences lower temperatures and shorter periods of exposure to "high" temperatures. The presence of water or ice affects evaporation by shielding. In winter, oil trapped in ice presumably undergoes no evaporation. For even the untrapped oil it is unlikely that there is significant evaporation because of low temperatures, the presence of ice and the blanketing effect of snow cover. It is also likely that sorption of oil on organic or mineral matter reduces the oil's effective vapour pressure.

The evaporation rate also depends to some extent on the soil porosity and permeability. Larger void fractions in the soil lead to larger porosity and permeability and thus faster rates of oil evaporation. Oil may also be absorbed in the interstices of porous material and thus be totally shielded from evaporation.

In summary, it appears that the dominant factors which control oil evaporation are:

i) the oil's inherent volatility characteristics;

ii) the time of exposure to evaporation as determined by depth, temperature and period of time from the spill;

iii) the oil content of the soil by influencing the thickness of oil pools or layers;

iv) the temperature, preferably weighted according to vapour pressure; and

v) the soil properties and thermal behaviour.

2.6 Novel Remedial Measures

As was discussed earlier, a number of remedial measures for site rehabilitation are available. A brief literature survey was conducted to determine if any novel *in situ* methods had been devised recently. McGill (1977) reviewed remedial measures for site rehabilitation such as addition of oil degrading organisms, nutrients, mixing or tillage, drainage and aeration. The only other methods known to be feasible are burning and water flooding; the latter has been discussed by Greene *et al* (1975) on the basis of some exploratory experiments by Mackay *et al* (1975). Little information on the burning of oils on soils was found, although some of the recent work on oil burning on ice and water may be relevant (Twardus, 1979). A body of information is available in the combustion literature on the behaviour of ground level fires, particularly, on rates of heat transfer by radiation and rates of flame propagation along liquid surfaces, but there are apparently no data on the burning of oil from a porous medium.

The mechanism of oil pool burning is believed to be that oil evaporates or boils at the pool surface as a result of radiative heat transfer from the flame above. The vapour then mixes with air in the flame and burns to carbon dioxide, carbon monoxide and soot, leaving the area in a hot buoyant smoke plume. The heat from the flame radiates to the evaporating pool, thus replenishing the fuel for the flame. When the oil pool becomes unable to sustain evaporation at the required rate, the flame tends to die leaving an involatile residue. This inability to evaporate may be due to the fundamental involatility of the residual oil, or to cooling by the substrate (especially if the substrate is ice) or in the case of soils, by the slow process of oil evaporation and vapour diffusion from the depths of the soil. It is thus possible that the fraction of the oil mass lost by burning in soils will be less than the mass lost by surface burning on, for example, water or ice. Ross *et al* (1977) have suggested that 10% to 50% of a crude oil may remain unburned under surface Beaufort Sea conditions.

2.7 Relationship Between Oil Degradation and "Toxicity"

Finally in this review, we speculate about the relationship between oil degradation and oil toxicity. "Degradation" includes all the previously discussed processes but is dominated in the short term by evaporation. "Toxicity" is used here as an ill-defined term characterising the oil's ability either to kill existing vegetation or to prevent reestablishment of vegetation. It is recognised that different species have different susceptibilities and that the more oil resistant species will tend to become established first. Presumably, the oil "toxicity" falls steadily as degradation proceeds until it reaches a level at which reestablishment of vegetation becomes possible. Since surface oil degrades faster than deep oil, it is likely that vegetation may become established at the surface while the underlying soil is still "toxic". Flooding of deep oil to the surface after heavy rainfall or as a result of traffic compression may cause recontamination of the surface and kill the establishing vegetation.

It would be invaluable to establish some relationship between degradation and a "toxicity threshold" since one could then calculate the expected degradation rate for a given spill site then assess the corresponding toxicity. This would enable revegetation measures to be implemented at the optimal time, i.e., when the "toxicity" has just fallen below the threshold into the "nontoxic" region. It would also provide a quantitative estimate of the rehabilitation time for a given situation and help determine whether this time is acceptable. Cases could arise where a 10 year rehabilitation time is judged to be unacceptable and soil removal and replacement is preferable.

It is believed that this approach of seeking information about the position of this "toxicity threshold" in terms of degradation provides a rational basis for forecasting recovery times and for determining when remedial measures should be implemented. The present work, being entirely physical in nature, cannot achieve this objective, but it is hoped that it can form the basis for future integrated physical-biological studies which could be successful.

A complication which is discussed in some detail later in this report and which has been noted by Rowell and McGill (1978) is that the successful establishment of vegetation is also affected by the physical condition of the soil which may have been substantially modified (adversely) by the oil. For example the soil's ability to transport water by capillary action may be reduced by the hydrophobic coating of oil. The lower albedo, due to surface darkening may also promote drier conditions.

2.8 Summary

It is apparent that when oil is spilled on a soil its behaviour is the result of a complex set of interacting processes including physical flow on and in the soil, biodegradation, dissolution and dispersion in groundwater, chemical reaction, sorption on organic or mineral matter and finally evaporation. It is important to gain some appreciation of the relative rates of these processes in order that those factors which limit rehabilitation rates can be identified and thus the most effective remedial measures suggested.

In this report most emphasis is placed on evaporation since it is believed to be an important short term process.

3. EXPERIMENTAL

3.1 1972-4 Experimental Spills

3.1.1 Methodology

Between 1972 and 1974 a number of experimental spills were undertaken at Norman Wells, Inuvik, Tuktoyaktuk and Richard's Island (NWT). Some of these spills were visited in 1976 and 1977, observations made and samples taken for analysis. In August, 1976, Mr. Wayne Toole visited the Norman Wells spills and the Richard's Island spill as part of this research program. In 1976, Mr. George Greene of Imperial Oil Ltd. (Calgary), who had been previously involved in the spill work kindly visited the Inuvik and Richard's Island sites and provided some photographs and samples at no expense to this research program.

The general procedure adopted during a visit was to observe the condition of the site, particularly the apparent presence or absence of oil by sight, touch and smell, and note the re-establishment of vegetation, take soil samples and photographs. It should be recognized that this does not represent a comprehensive and detailed site monitoring program, partly because of funding constraints, and partly because there remains considerable uncertainty about the optimal techniques for sampling and analysing oil-contaminated sites in the north.

3.1.2 Observations and Results

Details of the spill conditions and volumes have been provided in a previous ALUR report by Mackay, Charles and Phillips (1975). For all cases, Norman Wells crude oil was used as specified in that report.

1972 Norman Wells Spill

This spill took place in the summer of 1972 in a taiga forest near Norman Wells. The quantity of oil spilled was 0.72 m^3 and contaminated a surface area of 5.2 m^2 initially with an additional sub-surface area of 113 m^2 being affected.

In 1975, three years after the spill, some regrowth was evident on the contaminated area although the general appearance was brown and compacted.

In 1976 the effects of the oil were still apparent, however, regrowth was evident over the entire spill area. In regions where the soil was most heavily oil contaminated there was still relatively little growth with only occasional visible new vegetation. Areas which were lightly oiled and on which the oil did not reach the surface showed considerable growth and rehabilitation. It appears that on this site four years after the spill the oil has relatively little residual toxicity and the rate of recovery may be controlled by colonization processes. There are no overt signs of oil, indeed it proved impossible to obtain satisfactory oil samples from the soil because of the high degree of oil degradation. In 1975 it had been possible to take oil samples from this site and obtain gas chromatograms which, although showing signs of considerable weathering, still showed evidence of substantive quantities of oil. It appears that after four years the oil becomes essentially indistinguishable from the surrounding detritus.

It is noteworthy that over the entire spill area the average oil concentration was about 0.006 m^3/m^2 corresponding to an average oil "depth" of 6 mm. In the immediate vicinity of the spill the oil concentration was presumably much higher, possibly several centimetres. Compared with later spills this is a fairly light "oil exposure", i.e., the oil spread fairly thinly over the area and presumably the low quantity of oil resulted in faster evaporation. The three years required to reach the "toxicity threshold" may be atypically short.

1973 Norman Wells Spill

This spill was considerably larger than the 1972 spill consisting of 10.1 m^3 of oil spilled in a similar taiga forest site. The oil contaminated an area of 117 m^2 at the surface and an additional 200 m^2 were affected below the surface. The spill spread slightly thereafter possibly reaching an area of about 400 m^2. This corresponds to an average oil concentration of about 0.025 m^3/m^2 which corresponds to about 2.5 cm depth of oil, a factor of four higher than that of the 1972 site.

Visits in 1975 showed that there was little change in appearance of the spill two years after the event. The most devastated vegetation continued to be that which was directly contaminated by oil i.e. the vegetation lying in low lying areas. However, vegetation on higher hummocks appeared to be relatively unaffected, although the underlying detritus was oil contaminated.

In 1976 there was still overt evidence of oil in the form of black tarry soil especially close to the spill point. The general appearance of the vegetation was similar to that observed in the previous year. There was, however, some regrowth of vegetation in regions surrounding the spill especially on soil sites which had been contaminated only at depth. It appeared that the oil was still exerting a toxic effect on the vegetation and was hindering re-establishment. Some gas chromatographic analytical data from this site are shown in Table 3.1. It should be noted that the numbers presented in Table 3.1 are the relative amounts of oil in various carbon number ranges compared with all the material above C_{16} which is believed to be insensitive to evaporation. The four samples were taken at random from the spill area generally at a depth of 5-10 cm. As expected all the hydrocarbons below C_{10} had evaporated with only traces of C_{10} to C_{12} material remaining. There are still considerable quantities of C_{12} to C_{16} material remaining, i.e. typically about one-third of the amount originally spilled.

Interestingly, the column chromatographic analyses in Table 3.1 show that the saturates, which are generally regarded as the most biodegradable fraction of the oil have fallen relatively little. This is somewhat surprising and possibly indicates biodegradation is not as significant a mechanism of oil removal as is generally believed, at least in Arctic spills. The two final samples show a considerable increase in the insoluble nitrogen, sulphur and oxygen (NSO) compounds which may be either material originally present in oil or formed as a result of degradation of the asphaltenes or other hydrocarbons to oxygenated products. Experimental results show, as expected, a reduction in that ratio. However, the drop is not as large as might be expected from previous observations of oil degradation. For example the work of Green et al (1974) at Alert Bay showed a very significant

drop in the normal alkane to isoprenoid ratio whereas here the reduction is typically 45 to 75 percent. This suggests that oil trapped deep in the soil is biodegrading only very slowly.

1974 Richard's Island Spill

This spill on the tundra terrain consisted of 1.8 m^3 of oil and contaminated a surprisingly large area of 12.5 m^2 on the surface with an additional subsurface area of 320 m^2. This gave an overall contamination level of about 0.006 m^3/m^2 corresponding to 6 mm depth or about the level of 1972 spill.

A visit in 1975 showed relatively little change in the first year. In 1976, although there were still overt signs of oil on the site, there was considerable regrowth throughout the entire area. The site was visited in 1977 and regrowth was occurring even on the surface contaminated area. In general, the effect of the oil seems to be less pronounced than that at Norman Wells. The analysis of the oil samples shown in Table 3.1 show rather similar loss of volatiles and isoprenoid analysis. It should be noted that the Richard's Island spill was one year later than the Norman Wells spill.

3.1.3 Discussion

These results suggest that a typical history of a spill on taiga or tundra terrain may be as follows:

Immediately following the spill all the vegetation in direct contact with the crude oil suffers a lethal toxic effect. Presumably the incorporation of hydrocarbon into the plant material has a chemical and biological effect leading to death. Vegetation which is only contacted through the root system appears to be less affected although some species may experience delayed death. There is also the possibility that when high groundwater levels occur oil will be floated from the depth to the surface and contact hitherto uncontaminated vegetation.

The surface oil is subject to relatively fast evaporation and probably fast biodegradation. However, oil trapped at a depth of more than about 5 cm in the soil is shielded from evaporation and the rate of biodegradation of this deep oil appears to be very slow, possibly a factor of ten slower than that at the surface. This may be partly due to higher temperatures at the surface, photolytic effects on the oil, the presence of higher concentrations of nutrients and oxygen and differing bacterial populations.

The duration of the oil toxic effect is probably dependent on the amount of oil which enters the soil. A site which has been subjected to an oil concentration equivalent to a depth of about 6 mm apparently passes the "toxicity threshold" after about three years and revegetation then occurs presumably at a rate controlled by natural revegetation processes. At this time it is probable that additions of fertilizer and seeding would be advantageous.

If the oil concentration is higher, for example 20 to 30 mm as occurred in the 1973 Norman Wells spill, the oil remains toxic for at least

Table 3.1 Chromatographic Data from Spill Sites

Spill Site Sample	HYDROCARBON COMPOSITION C_1 -C_6	$>C_6$ -C_{10}	$>C_{10}$ -C_{12}	$>C_{12}$ -C_{16}	n-alkane/isoprenoid ratio $\frac{C_{17}}{\text{pristane}}$	$\frac{C_{18}}{\text{phytane}}$	% Saturates	% Aromatics	% NSO	% insol NSO
Fresh Norman Wells Crude Oil	56-63	156-183	51-67	92-103	1.01	1.22	-	-	-	-
Norman Wells Crude Oil 43% evaporated			2.1	78	1.03	1.21	55	30	9	6
Richard's Island 1974 Spill										
0 to 5 cm	-	-	-	34	0.62	0.63	-	-	-	-
5 to 10 cm	-	-	8	75	0.85	0.77	-	-	-	-
10 to 15 cm	-	2	7	77	0.92	0.75	-	-	-	-
15 to 20 cm	-	5	15	74	0.84	0.73	-	-	-	-
Norman Wells 1973 Spill										
0 to 5 cm	-	-	-	27	0.45	0.61	52	29	14	4
5 to 10 cm	-	-	0.8	53	0.60	0.84	55	28	12	5
10 to 15 cm	-	-	1.1	50	0.71	0.74	42	25	9	24
15 to 20 cm	-	-	-	30	0.73	0.75	35	30	15	20

four years. It will be interesting to monitor this spill and determine the duration of the toxic effect.

At none of these spill sites was any thermal instability observed. It appears that the insulating capacity of the active layer is not substantially affected by the presence of oil. It is probable that the albedo is reduced, resulting in a warmer surface. However, this effect is probably of the same order of magnitude as would occur in a taiga region as a result of a forest fire removing the tree canopy. Probably the most disruptive thermal effect would be that caused by heavy vehicular or foot traffic over the oil site. Previous recommendations that spill sites be subjected to minimal traffic appear to remain valid.

3.2 Field Studies of Oil Weathering and Burning in Ontario

3.2.1 Methodology

The outdoor oil spills on terrain were conducted at the University of Toronto's research station at Baie du Doré near Douglas Point on the shores of Lake Huron, Ontario. About three weeks prior to the spill, the site was prepared. Eight aluminum rings were constructed, 15 cm in depth with a perimeter of 4.83 m corresponding to a diameter of 1.54 m and an area of 1.86 m^2. The soil in the rings was the locally obtained top soil mixed with approximately 30 litres of peat moss per ring, thus giving a soil light in quality and fairly high in organic content. Some grass seeds, a mixture of Kentucky blue grass, creeping red fescue and rye grass, were sown in the soil and allowed to grow for about three weeks prior to the spill.

The spill took place on the 20th of July, 1977, in the afternoon when the temperature was 30°C and the winds were light at 16 to 20 km/hour. It should be noted that under these unusually hot conditions, the oil evaporated quickly. A total of 408 litres of Alberta mixed light sour blend oil was obtained from the BP refinery at Oakville and used in the test.

The general procedure was to measure a volume of oil and spill it evenly over the surface of the ring using a watering can. In some cases, oiled soil was ignited and in some cases fertilizer was added. The fertilizer was high nitrogen fertilizer containing 21% nitrogen, (of which 5.25% was water insoluble), 7.0% P_2O_5, and 7.0 % K_2O.

The variables which were judged worthy of investigation were three levels of oil dosage (i.e. litres/m^2), burning vs not burning and fertilizing vs not fertilizing. A complete experimental design with adequate replication would have required some twenty sites and approximately 1 m^3 (220 gallons) of oil - beyond the available resources. The study with only eight sites must be regarded as exploratory in nature rather than a definitive study of oil effects on soil.

The details of the various treatments are summarized in Table 3.2. For those sites to be burned the spill oil was allowed to soak into the soil for two minutes before ignition. Application of fertilizer to plots 1 and 5 was performed two hours after the previous operations had been completed.

Table 3.2 Oil Spills and Treatments of Various Plots

Number	Amount of Oil spilled (litres)	Burning after spilled	Duration of burning (minutes)	Amount of fertilizer added (g)
1	45	Yes, very vigorously	30	400
2	45	No	-	Nil
3	45	Yes, vigorously	7	Nil
4	22.5	No	-	Nil
5	45	No	-	400
6	67.5	No	-	Nil
7	67.5	Yes, fairly vigorously	20	Nil
8(A,B)	45	No	-	Nil

Plot 8 was designed to study the microbial activity and oil degradation. Half of this site (8A) was covered by a thin wooden sheet mounted about 15 cm above the soil surface to prevent direct sunlight from falling upon the soil surface. This was used to investigate the contention that microbial activity and oil degradation are enhanced by direct sunlight. Air movement over the soil surface was not significantly diminished.

The experimental design thus used three levels of oil, i.e. 22.5, 45 and 67.5 litres (5, 10 and 15 gallons) with the effect of varying quantity of oil being investigated as follows: Plot 4 with 22.5 litres, Plots 6 and 7 with 67.5 litres and the remainder with 45 litres. Plot 7 was burned, whereas Plot 6 was not burned. The effect of burning at both the 45 litre scale and the 67.5 litre scale on unfertilized plots is observable by comparing Plots 6 and 7 and Plots 3 and 8. The effect of fertilizing versus not fertilizing is obtainable by comparing Plots 1 and 3 which were burned and numbers 2 and 5 which were not burned. Finally, the covering of part of Plot 8 permits the sunlight effect to be examined in a rather cursory manner.

Because of the presence of a fire hazard in this area, (being close to a forest and the recent weather had been dry), there was some concern about starting a fire. The first site to be tested for burning (Plot 2) was allowed to lie for 15 minutes until the oil soaked fairly deeply into the soil. There were no pools of oil remaining on the surface, although the vegetation was quite wet with oil. Attempts to ignite the oil completely failed and it was decided to use this site as an unburned test. Subsequently, it was found that ignition had to take place within a few minutes of spilling, otherwise the loss of volatiles by evaporation and the loss of oil by permeation into the soil

precluded ignition. Generally, when there was no evidence of oil pools on the surface, it proved very difficult to ignite the oil. Once the oil was successfully ignited, there appeared to be some degree of evaporative "wicking" action whereby the oil deeper in the soil was induced to flow as vapour to the surface and there be ignited. It thus seems likely that the amount of oil effectively burned will depend on

i) the vertical penetration of oil into the soil;

ii) the time that has elapsed between the spill and ignition, and

iii) the ambient evaporation conditions and the volatility of the oil.

After fertilizing and burning, soil samples were taken from each area. These were taken using a soft drink can from which one end had been removed. The can was screwed into the soil, giving a sample about 10 cm deep and 5 cm in diameter. These samples were transferred quickly to plastic bags and sealed and stored in the refrigerator for subsequent analysis by gas chromatography.

In addition, a composite sample of the soil prior to the spill was taken and analysed for total density, moisture content, organic content and free volume. It should be emphasized that although every effort was made to make the soil samples homogeneous, there may be some site to site and within site variability in soil properties. The site was visited periodically in 1977 and 1978.

3.2.2 Observations and Results

It had been expected that some regrowth would occur on the sites in 1978, and to test the regrowth feasibility small quantities of grass seed were sown on the site periodically. In few cases was significant regrowth observed by the fall of 1978. On some sites small patches of grass began to grow from the bottom of the holes left after removal of the soil samples. On others, plants became established which, it was suspected, had root systems already present at the time of burning and well below the oiled level.

Most growth was evident on site 4 which was most lightly oiled (i.e. 22.5 litres). Considering the sites which had received 45 litres, most growth was on No. 5 where no burning had been attempted but fertilizer had been used. Sites 1, 2 and 3 were similar in that only small patches of grass had become established while Site 8 had no vegetation as had the two heavily oiled sites (6 and 7).

The sites were inspected again in August 1979, two years after the spill. There had been a general increase in vegetation but the herbicidal effects of oil were still evident. The heavily oiled sites (6 and 7) had still no growth; thus it was impossible to tell if burning had improved or retarded regeneration. The medium oiled sites showed considerable regrowth and it is believed that with tilling it would be difficult to detect any difference from an unoiled site. Most growth had occurred on Site 5 which was fertilized but not burned, followed by Site 2 which also was not burned but had not been fertilized. The burned sites (1 and 3)

had slightly less vegetation. The most lightly oiled site (4) had abundant vegetation.

3.2.3 Discussion

The results obtained, although only qualitative, agree with those obtained in the north. It appears that the oiled sites remain "toxic" and unable to support regrowth for at least one year and probably several years. Seeding during this period is of little use although fertilizing may be beneficial. It would be interesting to establish the reasons for this prolonged toxicity. Examination of the site and the seeds showed that the seeds had germinated. Some root growth was evident but all seedlings had died, for which several reasons can be advanced.

It is possible that the oil contains hydrocarbons which are herbicidal in nature. However, this effect is probably not strong at the soil surface for a long period because of the effective evaporation. The observation that some plants were able to grow through the oiled layer suggests that the toxic effect may not be strong. The regrowth at the bottom of the sample holes indicates that although the water in the soil may be contaminated with oil, the concentration is not sufficient to retard growth in regions very close to the oiled site.

Probably as important is the physical effect of the oil on the soil structure and ability to support growth. The oiled soil was darker, oily in appearance and apparently hydrophobic in character. A result may be that during hot dry weather the soil becomes dry and the seedlings become dessicated. Burning may aggravate this effect by reducing the amount of organic matter, and by forcing hot oil into the interstices of organic and mineral matter which was water logged at the time of the spill and would have resisted oil penetration. The lower surface albedo may also contribute to heating and drying. In support of this physical interpretation of toxicity is the observation that some oiled soil samples taken from the site and kept artifically wet in the laboratory in petri dishes were able to support grass seed germination and growth. The implication is that more attention should be paid to measures which restore the soil's physical structure rather than chemical condition. Obvious approaches are the incorporation of highly hydrophylic soils into the site at some appropriate time after the spill in order to improve water retention.

These Ontario results lead to a number of tentative and statistically insignificant inferences.

i) Oil spillage at a rate of 22.5 litres per plot (i.e. 0.012 m^3/m^2 or a 1.2 cm depth of oil) gives toxic conditions for 1 year but with substantial recovery in the second year. Probably after 2 years the site is essentially uncontaminated.

ii) Oil spillage at 45 litres per plot (i.e. 0.024 m^3/m^2 or a 2.4 cm depth of oil) gives toxic conditions which last into the second year but it is probable that after 3 years little effect is evident. Doubling the oil dosage appears to approximately double the the recovery time.

iii) At a spillage rate of 67.5 litres (i.e. 0.036 m^3/m^2 or a 3.6 cm depth of oil) toxic conditions last for over 2 years.

iv) The results indicate that burning may have a slight retarding effect on rehabilitation but the effect is certainly not measurable from these experiments. Fertilizing probably enhances the recovery rate but again the results are statistically insignificant. From a clean-up viewpoint, it seems that burning may be most desirable when the oil is in deep pools or is on frozen or water-logged soil. When the oil has permeated into the soil, burning may not be a useful technique. The studies by others on fertilizing indicate that the use of nitrogen and phosphorus supplements to restore a reasonable C-N-P balance is very desirable.

It is interesting to compare the Norman Wells and Ontario results for recovery time. An interpretation of the northern results is that the oil degrades to a "non-toxic" condition by evaporation, biodegradation and other processes at an effective rate of approximately 6 mm of oil in 3 years or 2 mm/year. Error limits on that rate are probably no larger than $\pm$ 1 mm/year. If the rate is constant, the 1973 spill may thus take 8 to 25 years to recover completely; the best estimate being 12 years.

The Ontario results yield higher rates of approximately 10 mm per year, a factor of five greater. This is probably attributable to the longer period of above 0°C weather in Ontario of 250 days compared to 135 days in the North which introduces a factor of approximately two. In addition, during the frost-free period ground temperatures are higher in Ontario, possibly resulting in a second doubling in rates. It would be interesting to study a series of similar spills under varying climatic conditions to elucidate the dependence of the rehabilitation rate on climate. Lacking such data, the best estimate which can be made at present, is that natural soil processes appear to be able to "detoxify" oil at a rate of 2 ± 1 mm/year in the Mackenzie Valley and 10 ± 3 mm/year in Southern Ontario. Some modest extrapolation to other conditions may be made, for example, as may apply in the Arctic Islands.

Finally, it is emphasised that these quantities must not be taken as accurately measured degradation rates. They are merely very approximate and simplistic estimates of the net rates of a multitude of complex, interacting physical and biological processes. Much further work will be necessary before rehabilitation rates can be predicted accurately from the local spill conditions. Perhaps the most useful contribution of this work is to indicate that a rational predictive method could be devised for estimating oil degradation and "detoxification" rates for various climatic regions and oil spillage rates.

3.3 Laboratory Studies of Oil Evaporation from Soils

3.3.1 Methodology

In view of the importance of evaporation early in the spill history and the apparently significant extent to which evaporation rates are reduced for oil which is trapped deep in soil, a number of experiments were undertaken to elucidate and quantify the rates at which oil evaporates from soil. Two sets of experiments were undertaken; the first being an exploratory study of oil evaporation from a deep container filled with soil; the second being a more precisely controlled experiment in which evaporation from sand beds was studied.

Natural Environmental Evaporation

In the first study two metal containers of 60 cm long by 60 cm wide by 30.5 cm deep were filled with a soil consisting of a mixture of 1 volume fine white sand and 3 volumes peat moss. Approximately 9 litres or 7.6 kg of Norman Wells crude oil were spilled evenly on the soil. The dosage was thus 21 kg/m^2 . These oil spill containers were located on the roof of the Wallberg Building, Department of Chemical Engineering and Applied Chemistry, University of Toronto, in a sheltered location. The temperatures, wind speed and rain/snow during the course of the experiment were recorded. The soil porosity was 0.49.

One hour after the spill, soil samples were taken by inserting a metal tube, 5 cm in diameter, vertically into the soil and about 7.5 cm of oil wet soil was removed. The sample was then divided into two portions: the surface 2.5 cm and the lower 5 cm, and were sealed in separate round bottom flasks.

The aim of sampling and analysis was to determine the extent to which each oil sample had evaporated, for example 20% mass loss. This is a difficult analysis since it involves first separating the oil from the soil without further evaporation, then analysis of the oil sample. A novel technique was devised which is fully described in Appendix I in which each soil sample was evacuated and the volatile crude oil condensed in two liquid nitrogen cold traps. These condensates were stored in teflon capped sample vials in a refrigerator. The residual soil sample was soxhlet extracted with benzene. The benzene extracts were first concentrated by means of a Büchi rotary evaporator and then stored in a vacuum dessicator to remove the last trace of benzene. All recovered oil samples were then analysed by gas chromatography.

Wind Tunnel Evaporation

In the second study a number of glass cylinders containing sand coated with synthetic oil were used. These cylinders were 8 cm inside diameter, 19 cm high, with a perforated metal bottom and contained 905 cm^3 of sand with a depth of 18 cm. The synthetic oil consisted of equal masses of n-octane, n-decane, n-dodecane and n-tetradecane (Kodak reagent grade). The density of this oil mixture was 744 kg/m^3. The proportions of the synthetic

oil and sand were found by trial and error such that the oil coated on the sand would not drip out from the perforated metal bottom of the cylinder after 5 hours. 905 ml of coarse sand (mesh 8-10) required 56 ml of the synthetic oil, while for finer sand (mesh 25-30) the same volume required 75 ml of oil. The coating was accomplished by shaking the sand and oil in a well-stoppered 2 litre conical flask. The sand was then transferred to the glass cylinders filling them to within 1 cm of the top. These cylinders were placed inside a wind tunnel in which the top surface of the sand experienced a steady current of air at constant wind speed and constant temperature. At regular intervals a glass cylinder and its contents was removed, the sand was divided into four equal layers (4.5 cm each) and each layer was extracted with 15-20 ml of n-pentane. The extract was left in a fume-hood until most of the pentane was evaporated. Its composition was then analyzed by gas chromatography to give the ratios of hydrocarbon peaks. From these ratios the extent of evaporation experienced by the oil could be determined. The void fraction of the fine sand was 0.37 and that of the coarse sand was 0.42.

The oil dosages or concentrations were thus for the fine sand 0.015 m^3/m^2 (1.5 cm depth) or 11.1 kg/m^2 and for the coarse sand 0.011 m^3/m^2 (1.1 cm depth) or 8.2 kg/m^2.

3.3.2 Development of Mathematical Model for Oil Evaporation from Soils

The objective of developing a model of oil evaporation from soil is to obtain a set of relatively simple equations which can be used to predict the rate at which a given quantity of a given oil will evaporate when spilled to a given depth in a soil. There are three aspects to this problem which must be quantified: (i) the volatility characteristics of the oil, which are fairly complex for a crude oil but simple for a pure hydrocarbon; (ii) the diffusive or transport properties of the soil and, (iii) the sorptive interactions between the oil and the soil. In view of the complexity of the problem the sorptive effect is ignored here. Further, constant temperature is assumed to apply at all times and depths and the soil is assumed to be homogeneous. Transport of oil by association with water is also ignored. The sorption simplification is not regarded as serious in the case of oil evaporation, where for example, the amount of oil is so large that sorptive effects are swamped. The interactions with water are slight because of the oil's low aqueous solubility. In treating the evaporation of more polar pesticides present in smaller quantities it would be essential to include such effects in any model.

The approach taken here is first to derive an expression for the volatility of the crude oil, and other petroleum products. It is then shown that the fraction of the oil which has evaporated is best expressed (for a given temperature) in terms of an "evaporative exposure" which is a combination of the oil's area per unit volume, the diffusive rate of removal of oil vapour from the oil surface, and time. Finally, the evaporative exposure is related to the condition and duration of the oil in the soil. For a given oil spill, the calculation of the fraction of oil evaporated at any given depth and time thus involves calculation of the exposure, then the oil fraction evaporated can be calculated for the assumed mean temperature and the given oil volatility.

Oil Volatility Characteristics

The following treatment is an outline of a more detailed approach which has been described by Mackay and Paterson (1979). The volatility of a liquid mixture (such as crude oil) can be expressed as a function of temperature T (K), an initial boiling point T_o (K) or an initial vapour pressure P_o (atm) and a constant C which characterises the fall of vapour pressure (or rise in boiling point) as evaporation proceeds. For pure liquids of constant vapour pressure during evaporation, C is zero.

It can be shown that C can be obtained from a plot of oil boiling point versus volume fraction distilled (F), the slope being $(T_E C/10.6)$ where T_E is the environmental temperature of interest. P_o can also be obtained from the boiling point curve by reading off the value for T_o directly and calculating P_o from it as

$$P_o = \exp\,(10.6\,(1 - T_o/T_E))$$

It can be shown that the oil's vapour pressure P_E can be calculated at any temperature and value of F from:

$$\ln P_E = \ln P_o - CF = 10.6\,(1 - T_o/T_E) - CF$$

where P_o and C are the values appropriate to the environmental temperature T_E.

A typical crude oil with an initial boiling point of 80^oC will have a P_o of 0.04 atm at 0^oC and a C value of 10.0.

Evaporative Exposure

When oil evaporates from a pool which is well mixed vertically it can be shown that the volume fraction of oil evaporated F depends on P_o, and C and an "evaporative exposure" E as follows:

$$F = (1/C).[\ln P_o + \ln(CE + 1/P_o)]$$

If C is zero the equation becomes:

$$F = EP_o$$

The group E has dimensions of atm^{-1} and is given by :

$$E = K_M Avt/RTV_o$$

where K_M is the evaporative mass transfer coefficient (m/s) (and depends primarily on wind speed), A is the spill area (m^2), v is the molar volume of the liquid which has evaporated (m^3/gmol), t is time (s), R is the gas constant (82×10^{-6} atm m^3/gmol K), T is temperature (K) and V_o is the oil volume (m^3). The group V_o/A is the slick thickness. The important feature of E is that it is linearly related to time.

The physical significance of E is that it can be regarded as the number of moles of vapour (both oil and air) which has left the spill per mole of oil originally in the spill. Thus if the liquid's vapour pressure is 1 atm and the liquid is pure, F becomes unity (all the oil evaporates) when E is unity. If P_E is 0.1 atm complete evaporation occurs when E is 10. For crude oils of low volatility E may be 100 or more for appreciable evaporation to occur.

These equations suggest an alternative approach to determining C and P_o by direct evaporation of oil in a pan in a wind tunnel. If the oil volume is monitored as a function of time and a pure liquid of known vapour pressure is evaporated simultaneously (to give K_M) a plot of F versus E can be constructed for an assumed value of v. Values of P_o and C can be fitted to that curve since P_o is the slope of dF/dE at E equal to zero and 1/C is the slope dF/dmE for large values of E, i.e. $E >> 1/CP_o$. A plot of F versus ln E or mt is thus expected to be approximately linear, an observation noted previously by Mackay et al (1975).

It may be desirable to generate a set of curves of F versus E for various temperatures of environmental interest.

For a pool of oil the calculation of fraction evaporated is thus straightforward, the oil properties are used to generate the constants P_o and C, the spill dimensions and time etc. give the exposure E, and F can then be calculated directly. For oil which has permeated into soil the situation is more complex in that a different expression must be used to calculate E.

Calculation of Exposure in Soils

For a pure liquid evaporating from a soil it is possible to generate an analytical solution for the evaporation rate. In practice, the liquid starts evaporating at the surface, removing liquid from the soil. An "evaporation front" thus moves vertically downwards, above which the soil is free from liquid, and below which the liquid is as yet unaffected by evaporation. The velocity of this front slows as it penetrates deeper because the vapour must diffuse over a larger path length with a correspondingly smaller concentration gradient. The delay time T(s) taken to reach depth Z (m) is:

$$T = Z^2 RTM/2D_E P$$

where M is the concentration of liquid in the soil (mol/m^3), D_E is the effective vapour diffusivity (m^2/s) and P is the liquid's vapour pressure. Interestingly, this is the same equation as describes ice thickness increase under freezing conditions if D_E is replaced by thermal conductivity and (RTM/P) is replaced by volumetric heat of fusion.

The exposure necessary to achieve complete evaporation at depth Z is 1/P or $(2D_E T/Z^2 RTM)$. A plot of E versus time gives E equal to zero until T when it rises instantaneously to 1/P. For an oil mixture this step change is changed to a more gentle sigmoid shape with evaporation of the more volatile material occurring before T and of the less volatile material occurring later. It is desirable to derive an expression for this sigmoid curve however analytical deviation is probably impossible and the result would be too complex to be used practically.

To obtain an expression it is first necessary to generate some exposure versus time curves. This was done by writing a computer program to perform a finite difference numerical integration of the evaporative behaviour of a two component system. The effects of the variables D_E, Z and M were investigated and the results fitted to give an empirical equation:

$$E = 0.6G \left(1 - \exp\left(-30 \left(GP_o\right)^2\right)\right) \left(1/\sqrt{GP_o}\right)$$

where $G = tD_E/Z^2 MRT$

The group G is the analogous quantity for soils to E for pool evaporation, the term MZ in G being equivalent to V_o/vA in E both being the number of moles of oil per m^2 of horizontal area. Both G and E have dimensions of atm^{-1}. Figure 3.1 is a plot showing the agreement between the empirical equation and the computed results.

This figure also illustrates the nature of the evaporation process and suggests that three regimes apply, each corresponding to dominance of a term in the above equation.

Considering for example the curve at 3.5 cm depth, the constants are such that at 1000 s G is approximately 12 and GP_o is approximately 0.08. At times shorter than this the exponential term $(1 - \exp(-30 (GP_o)^2))$ becomes very small. This regime corresponds to the delay time T which in this case

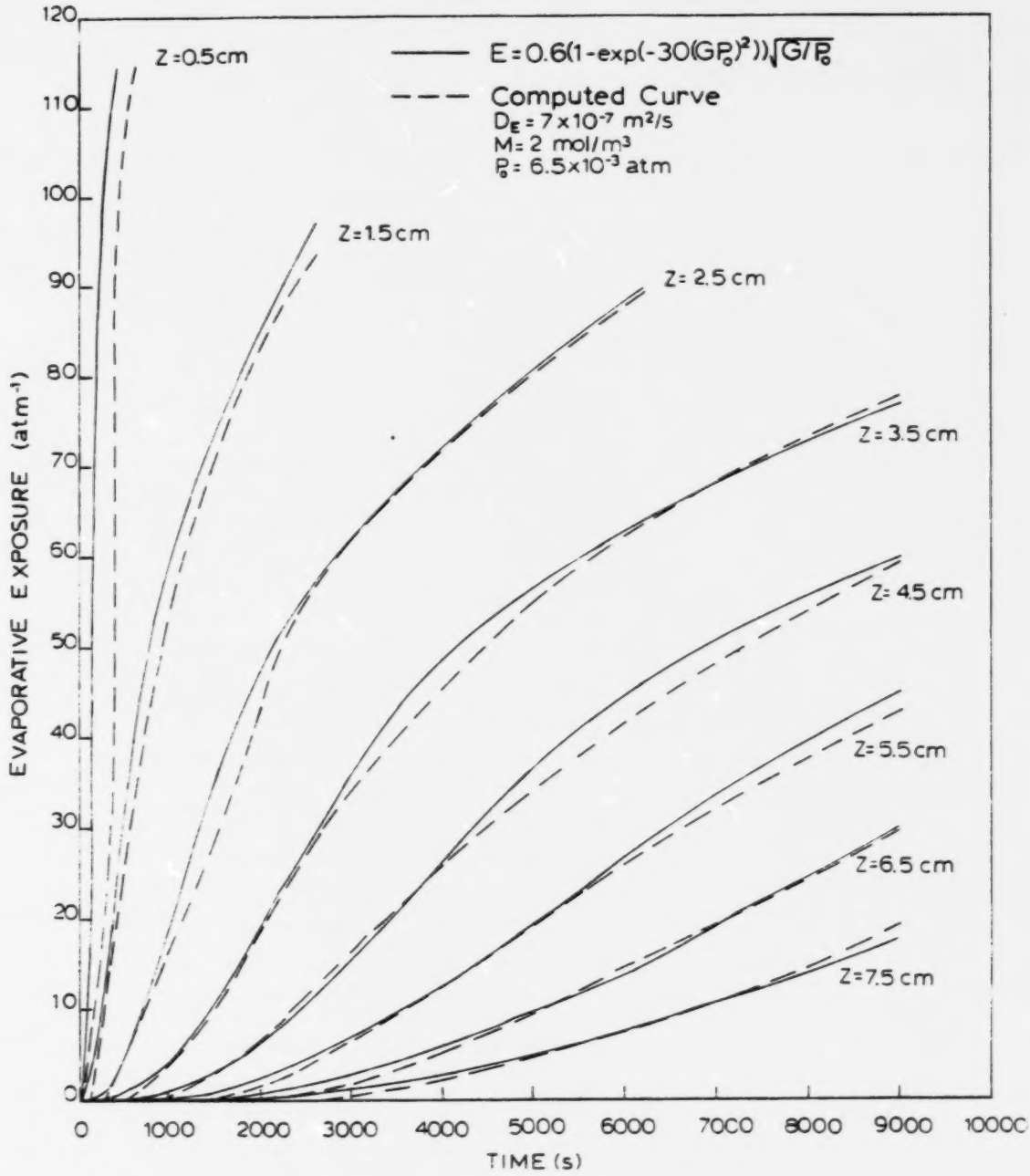

Figure 3.1. Comparison of computed exposures (from numerical simulation) with proposed equation

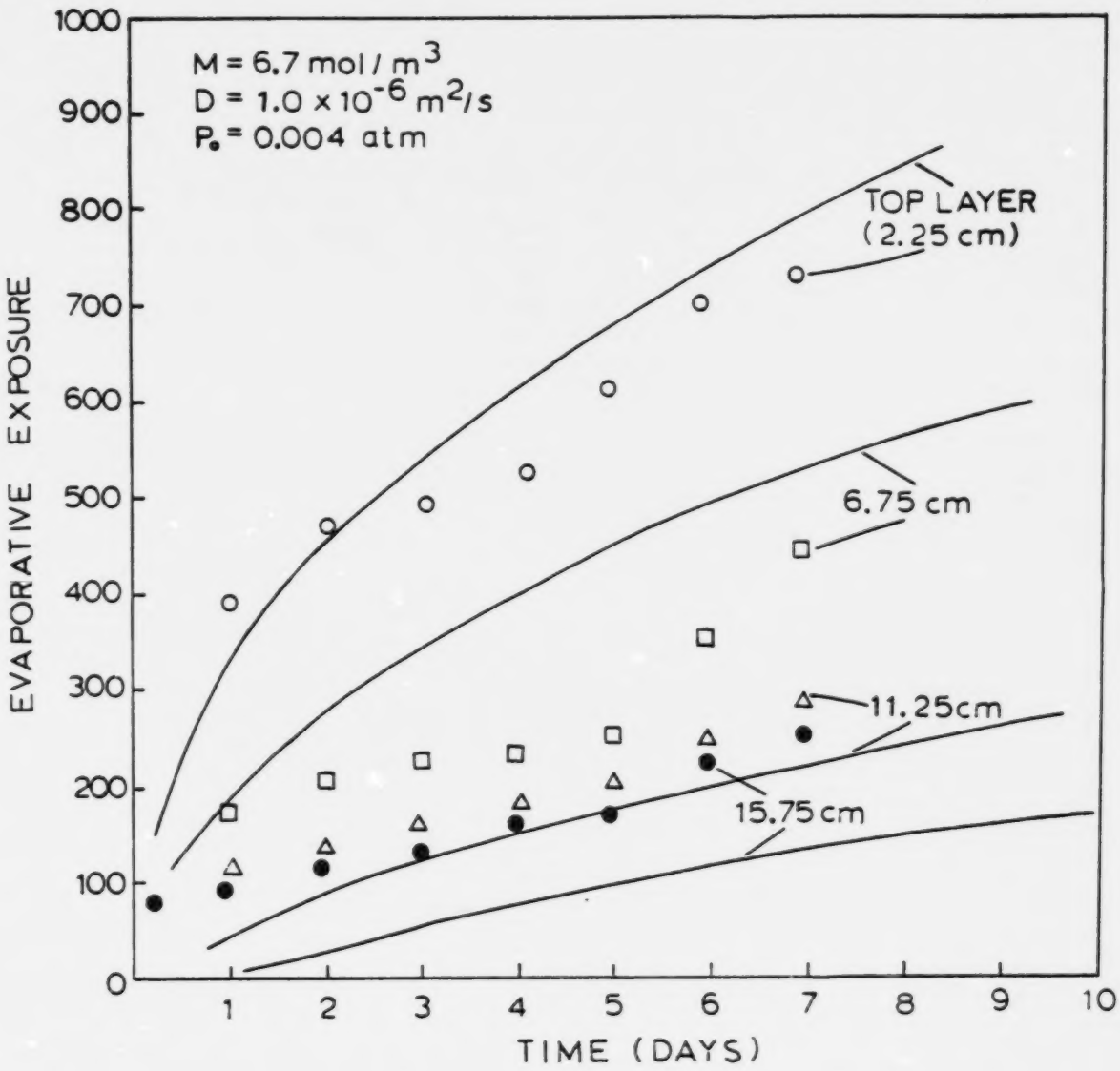

Figure 3.2. Comparison of experimental and predicted exposures for evaporation of oil from fine sand

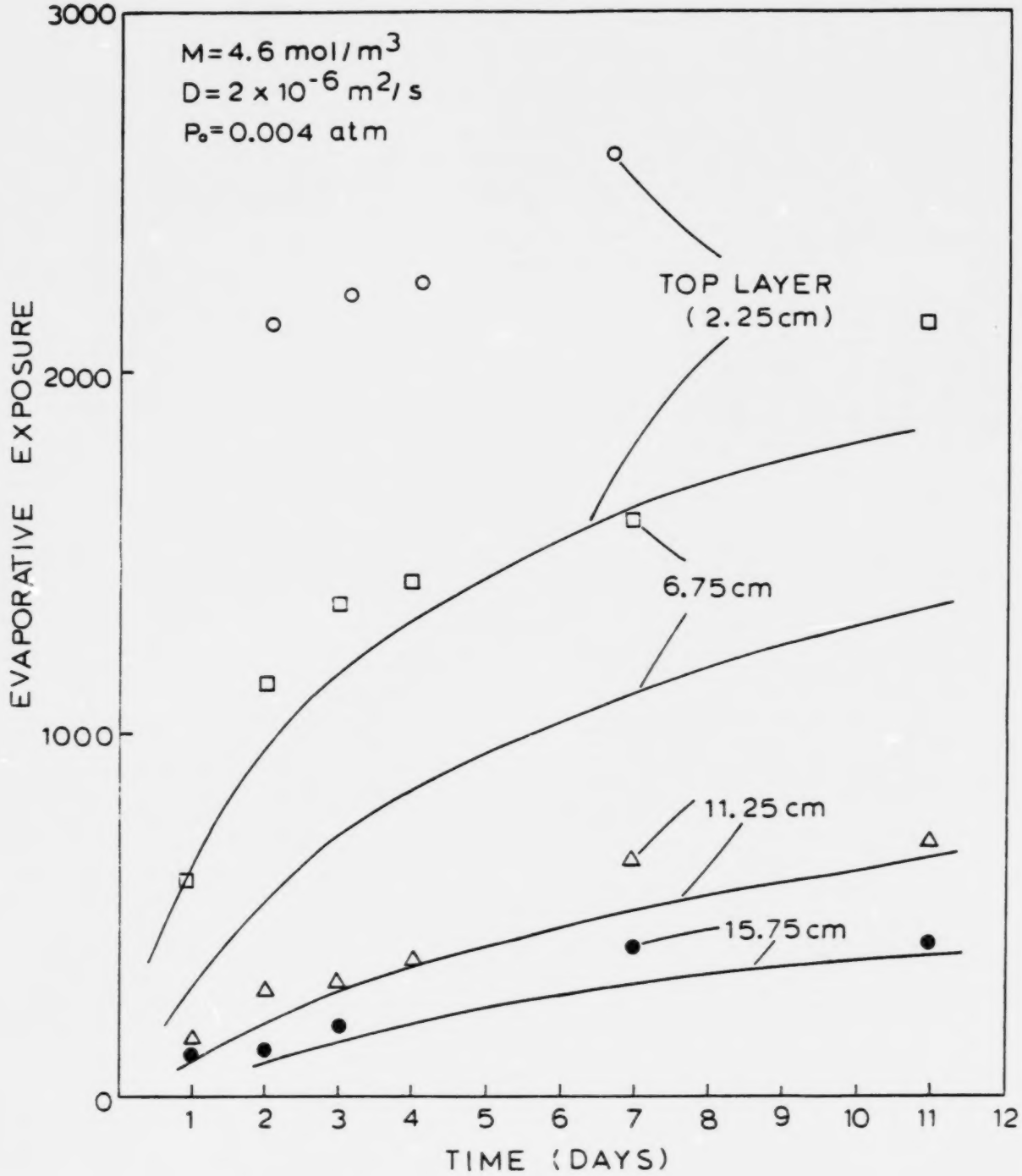

Figure 3.3. Comparison of experimental and predicted exposures for evaporation of oil from coarse sand

is approximately 1000 s at 3.5 cm depth. Only when GP_o reaches 0.2 does this term reach 0.7.

The second regime of active evaporation occurs when GP_o exceeds 0.2 until it reaches about 1.5 when E is approximately unity. At an E of unity for a pure liquid evaporation is complete.

Beyond this time active evaporation stops and the concentration is dominated by equilibrium from the vapour rising from the soil below. As GP_o increases the exposure E continues to increase but the term $(1/\sqrt{GP_o})$ becomes more significant.

Very little further evaporation occurs in this regime and it is of little practical interest because the oil is depleted of its more volatile material. Of greatest practical interest is the period of active evaporation when G and E have relatively similar values and GP_o lies in the range of 0.2 to 2.0. For a typical crude oil of P_o equal to 0.04 atm this corresponds to a G and E range from 5 to 50.

In summary, this equation enables estimates to be made of the evaporative behaviour of a typical crude oil in soils as follows. For the given oil, spillage conditions and diffusivity, the relationship between G, t and Z can be calculated as:

$$G = Kt/Z^2 \text{ where K is a constant.}$$

There will be a delay time at each depth corresponding to the time until GP_o reaches 0.2 or t becomes $0.2\ Z^2/KP_o$. Evaporation then proceeds "actively" until passive evaporation occurs.

Taking the Baie du Doré spills as an example, the soil effective diffusivity was believed to be approximately $7 \times 10^{-7} m^2/s$. The 45 litre spills corresponded to approximately 150 moles. Assuming penetration to 20 cm the oil concentration over the 1.86 m^2 plot (volume 0.372 m^3) was 400 mol/m^3 (i.e. M). Taking RT as 0.024 gives a constant K i.e. (D_E/MRT) of 7.3×10^{-8}. Since P_o was approximately 0.04 the delay times become:

$$t = 0.2\ Z^2/(7.3 \times 10^{-8} \times 0.04) = 6.8 \times 10^7\ Z^2$$

at 1 cm (Z = 0.01) t is 6850 s or nearly 2 hours. At 3.5 cm it is 1 day and at 10 cm it becomes 8 days.

Approximately 25% evaporation occurs for this oil when E is 30 (i.e. C = 10). This requires that G be 50 thus the time required is:

$$t = GZ^2/K = 50\ Z^2/7.3 \times 10^{-8} = 6.8 \times 10^8\ Z^2\ s.$$

At 1 cm this time is 19 hours, at 2 cm it is 3 days, at 5 cm it is 20 days, and at 10 cm it is 80 days. By contrast a pool of oil 1 cm thick would take about an hour to reach this extent of evaporation.

It may be useful to calculate a "retardation factor" by which the soil inhibits evaporation as compared to a pool, for the same oil spillage. An approximate "rule of thumb" is that most evaporation has occurred when E is 30, and G is 50. Substituting the typical values of K_M of 10^{-2} m/s,

D_E of 10^{-6} m^2/s and a penetration depth Z_M of 0.1 m and recalling that MZ_m is equivalent to V_o/Av:

For the pool: $E = 30 = K_M Avt_p/RTV_o$

For the soil: $G = 50 = t_s D_E/Z^2 MRT$

thus $t_s/t_p = (50\ Z^2 MRT/D_E)\ /\ (30\ V_o RT/K_M Av)$

$= 1.7 \times 10^4\ Z^2/Z_M = 1.7 \times 10^5\ Z^2$

When Z is 2.4 mm this ratio becomes unity and the oil at that depth evaporates as fast as in a pool. Oil closer to the surface evaporates faster in a soil. When Z is 1 cm the ratio becomes 17, at 5 cm it is 425 and at 10 cm if is 1700.

If the oil penetrates more deeply (Z_M increases) the effect is to reduce the oil concentration M. Thus the oil near the surface reaches a given extent of evaporation more rapidly (because less oil need evaporate) but oil close to the maximum penetration depth will take longer to evaporate. The implication is that it is desirable to minimize the penetration depth since this hastens evaporation and hence recovery.

The results of fitting the equation to the fine and coarse sand are given in Figures 3.2 and 3.3. The agreement between predicted and experimental values is satisfactory for the fine sand with there rarely being an error of over a factor of two. There is a consistent tendency for the lower layers to have evaporated faster than was predicted which may be due to evaporative loss from the samples during analysis. A considerable discrepancy exists for the surface layers of the coarse sand which is believed to be attributable to air currents which were set up in the sand as a result of wind movement.

Although these predicted evaporation rates are subject to error of the order of a factor of 1.5 to 2.0, it should be noted that no calculation of this type was previously possible and the actual physical conditions which the simple equations purport to represent are very complex and fundamentally incapable of accurate representation by simple algebraic equations. The equations appear to be the best available simple method of expressing oil evaporation rates from soils.

The effective diffusivity D_E is best measured for a given soil. However, an estimate can be made from the void fraction θ using a correlation below devised from the data of Satterfield and Sherwood (1963). This issue has also been treated by Penman (1940).

$$D_E = D_M \theta^{1.5}$$

where D_M is the molecular diffusivity.

4. DISCUSSION: IMPLICATIONS FOR REHABILITATION OF OILED SITES

The work described here, in conjunction with the literature on rehabilitation of oil contaminated sites can be used to suggest a number of principles which will be useful in mitigating the effects of terrestrial spills. These principles can be categorised into containment, oil removal, soil conditioning and revegetation. It is assumed that normal principles of prevention, early spill detection and cessation of spillage apply.

Containment

It is desirable to reduce the area of ground affected by oil. The options are to build dykes or containment dams from soil, snow, metal or wood or portable dams, or to trench the area such that the oil is diverted into a sacrificial area of containment. Some benefit may be obtained by diverting the oil into areas lined with oil-impervious plastic. It may be particularly desirable to prevent oil from reaching watercourses. Possibly the easiest condition to deal with is when the terrain is snow covered, the oil tending to sorb into the snow and become immobilized. If there is a substantial surface water flow in the area it may be necessary to separate oil from water in the containment area. During such containment activities it is desirable to minimize mechanical disturbance of the affected and unaffected terrain and it should be recognized that any exposure of permafrost may ultimately require remedial action.

It should be noted that oil can flow through the subsurface soil, possibly on water, for considerable distances then surface in depressions. Preventing such subsurface flow is clearly desirable and will usually involve trenching or insertion of sheeting.

Aspects of the containment problem have been reviewed by Greene et al. (1975) and Allen (1979).

Oil Removal

Oil present in pools several cm deep may be pumped to a vacuum truck or to drums and physically removed. Buhite (1979) for example has described the recovery of 15,500 barrels of oil from a 2.1 acre area following the sabotage of TransAlaska Pipeline in June 1977. Most of the remaining 500 barrels was burned.

It is obviously very difficult to recover oil which is present in thin slicks or which has penetrated into the soil. Some recovery can be achieved by flooding or flushing the area with water to induce the oil to float out of the soil. Any measure which brings oil to the surface is beneficial since surface degradation is much faster than that in the subsurface.

Burning (when it can be done safely) has been used successfully and, although some controversy remains about the long term recovery benefits, it appears that as long as the bulk of the soil is not substantially heated during burning, the effect is beneficial. If the soil is frozen or water logged, burning probably causes little harm. In dry soils burning may alter

the soil texture, induce deeper oil penetration, leave a toxic residue and kill deep rooted vegetation which could have survived oiling. The effect may thus be to retard recovery. It should be noted that burning is only likely to be feasible if the oil is ignited soon after spilling or it is in pools several mm thick. Weathered oil is difficult to ignite. Further, burning tends to destroy volatile oil which would be substantially lost in any event by evaporation.

Sorbents can also be used for oil recovery although experience with terrestrial spills is limited.

Soil Conditioning and Long Term Oil Removal

The available evidence suggests that the rate of long term recovery of the site is controlled by two factors, the rate of oil degradation (mainly by evaporation and biodegradation) and the physical condition of the soil.

Evaporation can be promoted by exposing the oil as much as possible to air movement. Measures such as tilling or gathering oiled soil into piles which are frequently turned over to "dry out" are desirable when there is no risk of thermal disturbance. If the terrain is subject to thermokarst development, it is preferable to leave the soil intact. Some benefit may be obtained by artificially drying the area by ground water diversion. The worst action is to compress the oiled soil since this reduces porosity (and hence evaporation) and destroys the soil's insulating capacity.

Biodegradation is best enhanced by applying fertilizer, high in nitrogen and especially phosphate (Westlake et al (1978), McKendrick and Mitchell (1978)). Application rates in the range of 500 to 1000 lb/acre (or kg/ha) are appropriate. The oil provides an abundant carbon source, thus the limiting elements for bacterial growth are likely to be first phosphorous and second nitrogen. The prevailing view is that bacterial seeding, i.e. the introduction of strains known to be hydrocarbon utilizing is unnecessary since such strains are usually present, will increase in numbers as conditions become favourable, and there is the potential for inadvertent proliferation of pathogenic (disease causing) bacteria by artificial introduction. It is likely that microbial breakdown will proceed rapidly and will have substantially degraded the oil after a few hundred days of above freezing aerated condition. In the north, of course with the relatively short summer, this may take several years. Fertilizer application should take place after physical oil removal is complete.

A condition which reduces both evaporation and biodegradation is when the soil becomes covered with a crust of relatively impermeable material or is waterlogged and anaerobic. This can occur by erroneously leaving containment dams in place. Rowell and McGill (1978) have documented such cases and have pointed out the need to maintain the soil in an aerated porous condition. If there is a strong incentive to rehabilitate the area rapidly it may be desirable to attempt to reduce the hydrophobic nature of the soil by mixing high organic soil in the surface, recognizing that the delivery and distribution of large quantities of soil may be in itself disruptive. If addition of soil is contemplated it is probably best to wait for a year to

allow evaporation to proceed unhindered by the additional diffusive resistance from the added soil.

During this longer term recovery period which may last 2 to 5 years, it is beneficial to minimize traffic across the contaminated terrain, even to the extent of fencing it. Periodic inspection to ensure that no substantial soil movement or interference has occurred is desirable.

Revegetation

In the long term the area will probably return to its original condition with the mix of plant species appropriate to the area. Although there will be natural seeding and recolonization, it may be desirable to seed artificially, preferably with fast growing species such as grasses which are native to the area and which are oil-tolerant. This subject has been reviewed in some detail by Hutchinson et al (1978).

Summary

In recent years a more quantitative understanding has emerged of the physical, chemical and biological processes which occur when oil is spilled on northern soils. Given this understanding a number of common-sense principles can be applied which have the general objective of enhancing the rates of the beneficial processes. Possibly the most important single principle is that in treating oil contaminated soils there is the potential to do more and longer term damage by well-meaning but ill-advised actions which involve substantial site disturbance. Often no action, or subtle actions, are preferable. The thoughtful application of remedial measures coupled to regular site inspection can probably hasten recovery, reduce clean-up costs and minimize environmental disruption.

Although it is impossible to predict oil degradation rates in soils with any accuracy, it appears that under Mackenzie Valley conditions, natural weathering and degradation processes are capable of "detoxifying" 2±1 mm depth of crude oil per year. This is approximately a factor of five slower than rates in Southern Ontario.

5. CONCLUSIONS AND RECOMMENDATIONS

The 1972 and 1974 experimental oil spills at Norman Wells, Inuvik, Tuktoyaktuk and Richard's Island have provided, and continue to provide, valuable data on the rates of degradation of oil and on the revegetation process. None of these spill sites shows any evidence of thermal instability. The results from monitoring these sites indicate that for an oil concentration of 0.006 m^3/m^2 (corresponding to an average depth of 6 mm), there is about a 3 year period in which the oil is readily detectable and vegetation regrowth is prevented. After about 3 years (at Norman Wells), the surface soil is essentially oil-free. It is suspected that high oil concentrations will result in prolonged periods of the toxicity as a result of longer persistence of the oil.

A number of test plots have been set up at the Baie du Doré experimental station in Ontario and subjected to oil contamination at various levels. Some of these plots have been burned, and some fertilized. Some regrowth took place following seeding in the most lightly oiled plots, but no substantial regrowth took place on the other plots. Burning has had no significant beneficial effect. It is recommended that these sites be monitored to elucidate chemical changes in the oil and to assess their revegetation potential.

It is believed that the capacity of the oil-contaminated soil to support newly establishing vegetation is largely controlled by the presence of toxic oil components (which are removed by the natural processes of evaporation and biodegradation) and by the physical condition of the soil, particularly its oil-induced hydrophobic character which adversely affects water retention. Measures which promote evaporation and biodegradation and which restore the soil condition are obviously beneficial.

Sampling and analytical procedures have been developed for monitoring the physical and chemical changes which occur to oil spilled on soils. A novel feature of this procedure is the use of vapour extraction of oil from soil samples. This permits the quantitative recovery of volatile hydrocarbons which could not be analysed by previous liquid extraction procedures.

Laboratory experiments on the rate of evaporation of oils from soils have resulted in the postulation of an equation which permits for the first time, the degree of oil evaporation to be estimated at various times and soil depths. The laboratory data have provided an estimate of the values of the parameters in this equation. It is recommended that further, and more accurate, determinations be made in order to validate the equation and provide more reliable data on the dependence of weathering rate of factors such as temperature, soil type, porosity, and degree of oil contamination.

A brief review has been presented in which the implications of the experimental programs for recovery of oil-contaminated sites are discussed and recommendations are made for procedures which will enhance recovery rates.

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APPENDIX 1

Analytical Methods Development

The problem addressed here is that of taking a representative sample of the soil, transporting and storing it until analysis, such that it is not significantly affected during these processes and finally subjecting it to a number of analytical techniques which will yield data about the change in composition of the oil components. This process is difficult by virtue of the intimate contact between the oil and the soil, which may be sorptive in nature. The soil may contain other organic materials which will interfere. Crude oil is unfortunately a very complex mixture of hydrocarbons, only a few of which can be determined individually. Thus the data obtained provide only approximate or average indications of the extent of physical or chemical converstion or modification. The most powerful analytical tool is gas chromatography (GC) which is used here for two purposes; first, separation of the crude oil according to volatility or boiling point providing data on the extent to which the material has been subjected to evaporation. Second, analysis of the isoprenoid components, pristane and phytane (which are reputedly only very slowly biodegraded by microorganisms) and the neighbouring normal alkane compounds which are readily degraded. Examination of the ratio of the normal alkanes to isoprenoids gives information about the extent to which microorganisms have been successful in degrading the oil. This technique has been widely used, for example, by Cook and Westlake (1975) for soils and by Greene et al (1975) for a shoreline spill at Alert Bay (NWT).

It is believed that classes of hydrocarbons, for example, alkanes, aromatics, asphaltenes and nitrogen, sulphur and oxygen (NSO) compounds will behave differently in a soil environment. Separation into these classes is possible using column chromatography, for example, following the procedure of Cook and Westlake (1975). The eluates from this procedure can be weighed, thus giving an estimate of the proportions of these compounds present in the sample and each individual eluate can be subjected to gas chromatographic analysis in order to determine its volatility characteristics. Unfortunately, the procedure inevitably results in the loss of some volatile material, however, this can be taken into account if a standardized procedure is adopted.

Since volatile hydrocarbons are often the most toxic and soluble, and they are also likely to be the hydrocarbons most susceptible to burning, it is important to have a reliable method of estimating the quantity of residual volatile hydrocarbon in a soil sample. The extent to which a sample has been subjected to evaporation can be measured by examining the ratio of the amount of volatile to non-volatile material in various carbon number groupings. This ratio will generally fall as the oil is subjected to evaporation and if it is assumed that the non-volatile material is lost by other non-evaporative processes at the same rate as the volatile material then the extent of evaporation can be calculated. This analysis is difficult because the conventional extraction procedure involves the dissolution of the oil in a hydrocarbon (usually benzene or pentane) and subsequent evaporation of that solution to concentrate the extract. During this evaporation, an indeterminate amount of the volatile material is lost, thus such liquid extraction techniques for soil samples are fundamentally unsuited as a method of determining volatile hydrocarbons. A

method was devised as part of this work in which the samplewas "distilled" under reduced pressure and at slightly elevated temperatures (i.e. 40°C) to evaporate any volatile hydrocarbon, the vapours being collected in a liquid nitrogen cold trap. This removes from the sample all the hydrocarbons up to about C_{12} and yields a volatile sample which can be analysed separately, both for total mass and composition. The residue is then extracted either by shaking with benzene or by soxhlet extraction and the extract evaporated to "dryness" with no fear of loss of volatiles.

It is obviously important to take the sample, store it and transport it in a reproducible manner. For this reason, a standard procedure was worked out. Figure A1 shows the gas chromatogram of the fresh crude oil (Norman Wells) while Figure A2 shows the superimposed gas chromatograms of the same oil extracted from soil using the methods discussed above. The volatile extract can be analysed separately or it can be added to the liquid extract (after the latter has been subjected to solvent removal by evaporation) and the mixture analysed. Figure A2 shows that adding the two extracts yields approximately the parent oil. Compounds in the C_9 to C_{10} range lie in the intermediate region present in both extracts. This range can be varied by adjusting the volatile extraction temperature and time. Careful examination of volatile fraction shows that practically all of the hydrocarbon components above C_5 can be recovered, while those below C_5 are mostly gases dissolved in crude oil and their recovery is extremely difficult.

When the extraction conditions are the same, the extent of weathering for different samples can be compared by simply comparing the gas chromatograms of the volatile fraction. Similarly, the biodegradation of the various samples can be compared by studying the isoprenoids peaks in the chromatograms.

Analytical Procedures

Sampling

The soil sample should be taken with a sharp metal tube (made from a pop can) about 5 cm diameter which is "screwed" into the soil. The core is removed intact and ejected, then sectioned into a number of horizontal layers with a sharp knife. The soil samples are sealed inside small polyethylene bags. The samples are kept at a low temperature (e.g. 0°C) prior to analysis. The mass of each sample should be recorded.

Vacuum Extraction

An air tight container with the oiled soil is connected to a vacuum pump through a series of cold traps. The system is exercised to prevent losses during evacuation, by giving sufficient time for the volatile crude oil to condense inside the liquid nitrogen traps. The oiled soil and its container is shaken occasionally to facilitate extraction. At the end of the vacuum extraction, the condensate is allowed to thaw and then recondensed into one trap. This collected fraction is then transferred quickly into a vial at room temperature and analyzed by gas chromatograph, preferably immediately. All samples are stored cold to prevent any losses.

The less volatile crude oil in the wet soil is recovered by soxhlet extraction with benzene as solvent. The benzene extract is then concentrated

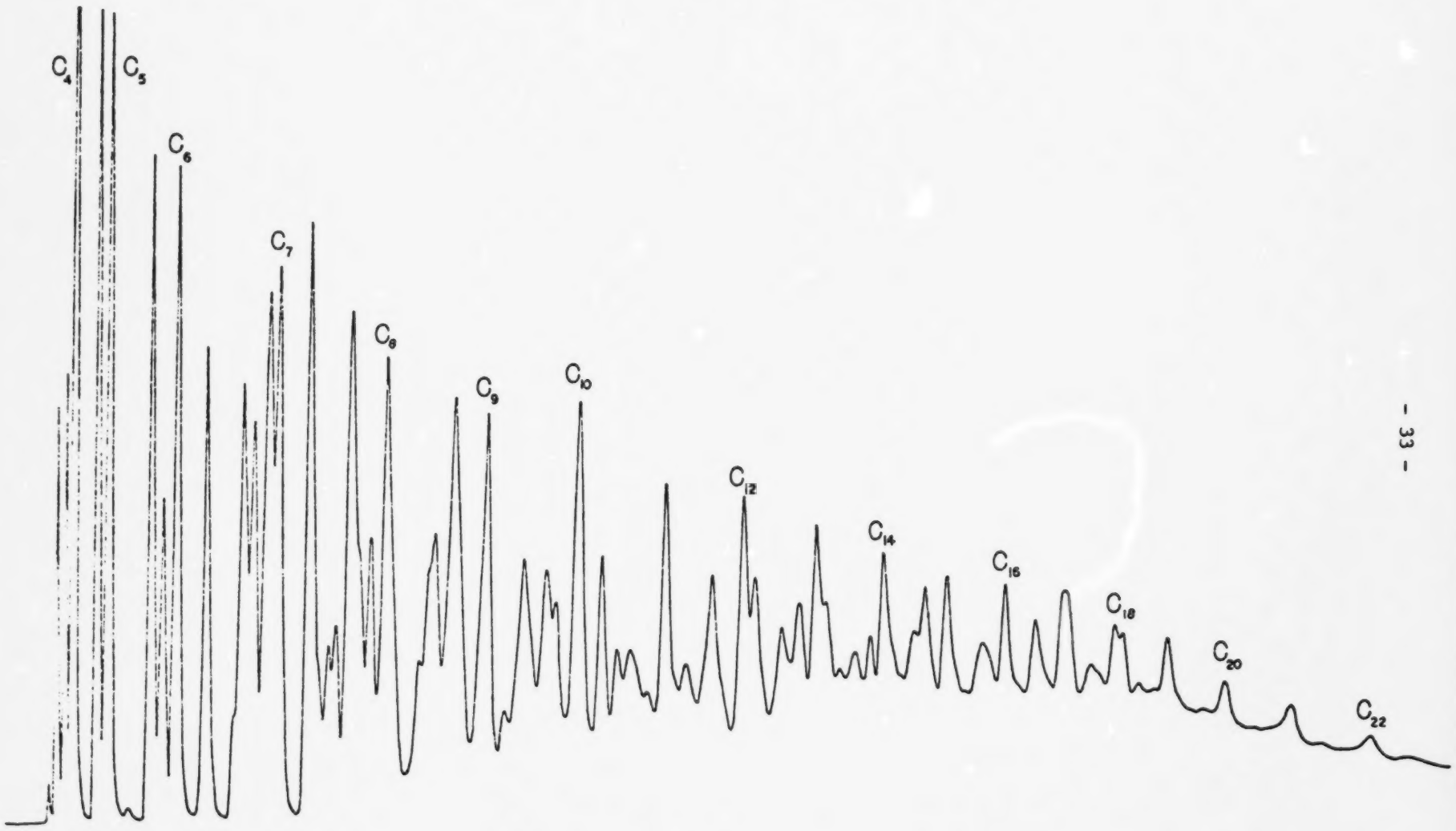

Figure A1. Gas chromatogram of fresh Norman Wells crude oil

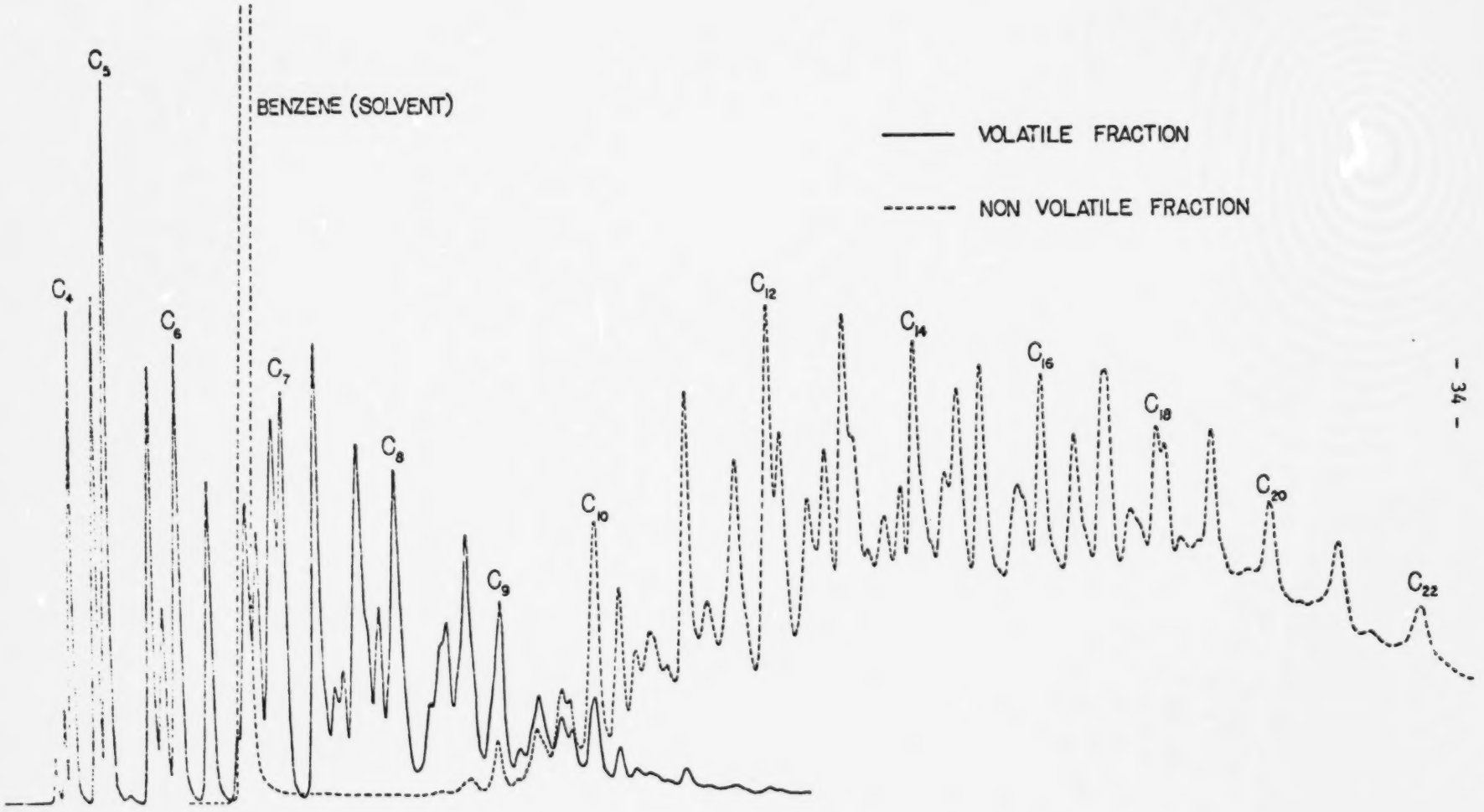

Figure A2. Gas chromatograms of extracted Norman Wells crude oil mixed with soil

by means of a Büchi rotatory evaporator and stored in a vacuum dessicator to remove the last trace of benzene.

Gas Chromatographic Analysis of Crude Oil or Petroleum

The gas-liquid chromatographic analysis was done on a Hewlett-Packard Model 5750 gas chromatograph equipped with a flame ionization detector. Peak areas were determined by a Hewlett-Packard Model 3371 B Electronic Integrator. The system was programmed from 50 - 280°C, increasing the temperature 15° per minute, with a 1 minute post injection time. Injection sample sizes were 0.5 µl in volume.

Specifications

Columns - stainless steel dual columns
- 3 m long, 3.2 mm inside diameter
- packed with 10% SE 30 Ultraphase Chromosorb P, AW-DMCS, Mesh 60/80

Injection temperature - 300°C

Detector temperature - 325°C

Gas flow rates - helium 40 ml/min
hydrogen 35 ml/min
air 500 ml/min

Liquid Extraction of Crude Oil from Soil

The extraction of oil from experimental soils was accomplished, by shaking each 4 cm thick layer in a 250 ml erlenmeyer flask, with enough n-pentane ("Distilled in glass" - Caledon) to completely immerse the soil. These flasks were gently shaken for 6 days, after which the n-pentane solution was decanted off. The residual soil was rinsed continually with n-pentane until it decanted clear.

The extract was vacuum filtered through Type SM 5 µm filter paper, and then let stand in a fume hood until all the excess n-pentane had evaporated (1-3 days). Each sample extract was then stored for analysis in a 7 ml specimen bottle.

Liquid Chromatographic Fractionation

The liquid chromatographic fractionation was carried out in a 1 x 40 cm dual phase column. The bottom half of the column was packed with 10± 0.2 g of activated 28/200 mesh silica gel (Fisher Scientific). The upper half of the column contained 10 ± 0.2 g of activated F-20 alumina gel (Alcoa). Both phases were suspended in n-pentane ("distilled in glass" - Caledon). The oil was carefully layered on the top of the column and then eluted sequentially with 65 ml of n-pentane, 100 ml of benzene and 100 ml of a 1:1 mixture of benzene-methanol (ACS spectro grade - Caledon). This procedure eluted the saturate, aromatic, and soluble NSO(nitrogen, sulfur, and oxygen containing hydrocarbons) components in that order. The sum of these three weights subtracted from the weight originally applied to the dual phase column yielded the insoluble NSO component weight. The NSO components were not considered in this study.

The fractions of interest were then subjected to G.C. analysis.

Gas Chromatographic Analysis of C_{17} and C_{18}

The gas-liquid chromatographic analysis of the pristane-C_{17}, and phytane-C_{18} ratio was done on an HP 5700A gas chromatograph with an HP 3380A integrator. The system was temperature programmed from 50-220°C, by increasing the temperature stepwise 5° per minute. Injection sample sizes were 0.9 µl with an injection spitter allowing 1/50 into the column.

Specifications

Columns - stainless steel open tubular column, coated with 7% OV-101
- 22 m long, 0.25 mm inside diameter

Injector temperature - 300 °C

Detector temperature - 350 °C

Gas flow rates - helium 4 ml/min
hydrogen 30 ml/min
air 240 ml/min
aux. helium 30 ml/min

APPENDIX 2

Guidelines for Rehabilitation of Oiled Sites

This appendix consists of a straightforward set of guidelines written in non-scientific language which, it is hoped, will be useful to those engaged in the practical aspects of clean up and rehabilitation of oiled sites.

1) Stop the Source

The obvious first step when an oil spillage is detected is to stop the spill at the source whether it be a pipeline or tank. This can be accomplished by blocking the oil leakage or by pumping the contents elsewhere, for example into tank trucks. This operation is normally the responsibility of the operator of the oil-containing facility. Particular attention must be paid to avoiding fires and explosions. Crude oil and gasoline are highly flammable and vapour clouds can explode thus it is wise to keep well away from the oil. Heavier fuel oils are less dangerous but there remains the possibility of personnel being trapped and burned if the oil is ignited. No actions should be taken which risk human life.

2) Contain the spill in as small an area as possible

The oil will flow on the land surface and possibly penetrate into the ground, flowing of course in a downhill direction. By examining the slope of the land it should be possible to determine where the oil will flow and decide upon an area in which it can be dammed and contained. The total volume of oil spilled should be taken into account i.e. ensure that the dammed area is big enough to accept all the oil and will not overflow. Also, avoid areas where there is much flow of water since the water will fill the dam and cause the oil to overflow. Avoid having the oil enter creeks or rivers.

Damming can be accomplished by trenching by use of soil, gravel or sand or even snow in winter. Plastic sheeting can be used to stop oil penetrating into sand or gravel. Other barriers such as wood or metal sheet can be used if they are available locally. Try to insert sheets of wood, metal or plastic as deeply as possible to prevent oil from soaking under them.

The aim is to use whatever materials are available locally to stop the oil spreading as quickly as possible and contain it in a small area. It is much easier to recover and remove the oil if it is confined to a deep pool in a small area.

Try to scare birds and other wildlife out of the area because it is likely that if oiled they may later die by exposure or by ingesting the oil in an attempt to remove it.

3) Remove the oil

The best procedure is to suck or pump the oil from the pool into a tank truck. Some trucks have vacuum systems which can be used to suck the oil from the pool. It may be necessary to connect up a gasoline or electrically driven pump. Try to draw up as little water as possible. Remember that a pool of water with an inch of oil floating on it looks as if it is all oil. Scooping out a volume in a glass vessel or bottle will show if much water is present.

If a truck is not available a temporary storage tank can be used. This can be metal, or a flexible bladder tank or even an improvised tank made from plastic sheet.

It becomes very difficult to remove oil when it has soaked into the ground or it is present as shallow pools. It may help to pump water through the oiled area to "wash out" the oil, provided that the water will not cause the oil to flow away.

Separating oil from water can be done if the water can be drained or drawn off or siphoned from under the oil layer. It is usually necessary to keep a close watch on such separating systems since the oil may drain away with the water.

4) Burning

If the oil can not be removed it may be burned as long as the soil under the fire will not be burned appreciably. If the soil is water logged or contains ice it is unlikely that it will be seriously affected by the fire. If the soil is dry it is probable that the fire will do as much damage to vegetation as the oil. If there is no vegetation the fire will do no harm. If the oil has had time to evaporate it may be difficult to ignite and some kerosene may be used to get it started. Do not use gasoline - it is too dangerous. Remember that oil fires will burn and spread rapidly thus under no circumstances should a fire be started if there is any risk of starting a forest fire or burning buildings or storage tanks.

Burn only when the fire can be completely controlled and the ground under the fire either has no vegetation or the vegetation is protected from the heat.

Remember that fires can be very dangerous.

5) Absorbing the Oil

Sometimes it may be possible to absorb the oil into a porous material such as moss, straw or even snow then remove the oily material by hand for disposal at a dump. Commercial sorbents are available but they are usually quite expensive.

6) Oil Disposal

If the oil can be returned to its owner it can often be cleaned up and recovered. If not, the oil and oily material is best disposed of by burning, preferably at an approved dump. Precautions should be taken to ensure that the oil is not accidentally ignited during transporting or dumping.

7) Rehabilitation of the Site

After the oil is removed the site should be rehabilitated to as close to its original condition as possible with any dams removed and trenches filled. This is particularly important in permafrost areas. Avoid making any changes to the drainage pattern of the site.

Unfortunately there have been many instances of more damage being done by trenching, damming and generally disturbing the ground by vehicles than would have been done by the oil if left alone.

There is probably little merit in adding fertilizer or seeding until the oil has had a chance to evaporate over a period of at least two months of above-freezing weather. The best procedure is to assist the soil bacteria to break down the oil by providing nitrogen and phosphate fertilizer. A high nitrogen and phosphate fertilizer applied annually at 500 to 1000 lb/acre is recommended. After one growing season it may be desirable to seed the area with grasses which grow naturally in the area. If the seed is applied too early the oil may still be toxic and the seed will not grow. A small test plot can be established to determine when the toxicity of the oil has fallen sufficiently for the soil to sustain growth.

It will probably take many years for the site to return to close to its original condition. Periodic inspection, fertilizing and seeding is very desirable. Efforts should be made to keep traffic off the site by signs and even fences. It is advantageous to keep the soil aerated as much as possible to encourage bacterial action. It may thus be desirable to drain depressed areas.

In extreme cases when it is important to rehabilitate the site rapidly it may be necessary to remove and dump the oily soil and replace it with uncontaminated soil.

For scientific purposes it would be very helpful if a sample of the spilled oil would be taken in a glass bottle filled almost to the top (i.e. < 10% air space) and well sealed and stored in a refrigerator. From the nature of the oil, a knowledge of the amount spilled and the clean up and rehabilitation measures taken it is possible that better procedures can be suggested. It is thus very desirable to document the events as completely as possible.

Finally, all clean up and rehabilitation measures should be taken with the approval and advice of the appropriate local government agencies.